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Low Band Gap Planar Conjugated Pyrrole-Derived Polymers. Optical Absorbances From the UV to the Near-IR

by

T. W. Brockmann and J. M. Tour

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Department of Chemistry and Biochemistry  
University of South Carolina  
Columbia, SC 29208

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13. ABSTRACT (Maximum 200 words)  Described will be the synthesis of a pyrrole-derived polymer that can exist in a zwitterionic form ( $\lambda$ = 520 nm), a partially reduced form ( $\lambda$ = 290 nm), or a planar form ( $\lambda$ = 900 nm). The absorptions are reversible depending on the pH of the medium.					
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# Low Band Gap Planar Conjugated Pyrrole-Derived Polymers. Optical Absorbances From the UV to the Near-IR

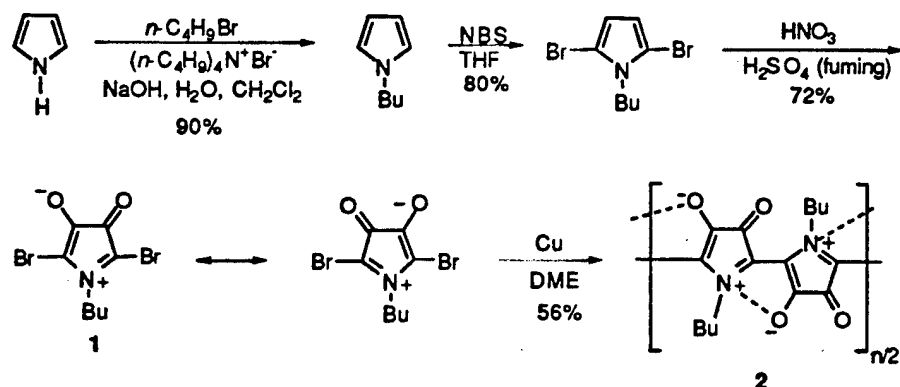
Thorsten W. Brockmann and James M. Tour\*

Department of Chemistry and Biochemistry  
University of South Carolina  
Columbia, South Carolina 29208

In an effort to maximize the extended  $\pi$ -conjugation in polymers and to study their corresponding electronic and optical properties, several have undertaken the synthesis of new conjugated organic polymers that have a planar or near-planar conformation between the consecutive repeat units.<sup>1,2</sup> Described here is the synthesis of a unique zwitterionic pyrrole-derived polymer that can reversibly convert to a linear and planar conjugated polymer with a solution band gap of approximately 1.1 eV. The material possesses a reversible and enormous pH-dependent or solvent dependent absorption spectral range from the UV to the near-IR spectral region. Soluble polymeric materials that can respond dramatically and reversibly to external stimuli could have importance in the development of organic-based optical and electronic sensors,<sup>2</sup> while polymers with absorbances in the near-IR can serve as dyes for optical data discs.<sup>3</sup>

The synthesis of the new pyrrole-derived zwitterionic polymer is described in Scheme 1.

Scheme 1



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Pyrrole was N-alkylated under standard phase transfer conditions.<sup>4</sup> Bromination<sup>5</sup> and vigorous oxidation yielded the zwitterionic monomer **1**, a carbonyl-stabilized azomethine ylide, in an overall 52% yield for the three steps. The FTIR (KBr, 1718  $\text{cm}^{-1}$ , with no hydroxyl absorbance), mass spectrum (calc'd for  $\text{C}_8\text{H}_9\text{Br}_2\text{NO}_2$ : 311; found: 311), elemental analysis (calc'd: C, 30.89; H, 2.92; Br, 51.39; N, 4.50; found: C, 30.90; H, 2.92; Br, 51.25; N, 4.48), UV spectrum ( $\text{CH}_2\text{Cl}_2$ ,  $\lambda = 248, 322$ ; NMP,  $\lambda = 281, 320$  (sh); there was little change in the UV spectra in the presence of aqueous NaOH or aqueous HCl),  $^1\text{H}$  NMR [(300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.59 (t,  $J = 7.3$  Hz, 2 H), 1.57 (p,  $J = 7.1$  Hz, 2 H), 1.30 (sext,  $J = 7.3$  Hz, 2 H), 0.91 (t,  $J = 7.3$  Hz, 3 H)] and  $^{13}\text{C}$  NMR [(75 MHz,  $\text{CDCl}_3$ )  $\delta$  163.85, 129.24, 39.48, 30.39, 19.82, 13.52] were all consistent with the proposed structure. Note that two resonance forms exist for **1**, therefore there are only six peaks in the  $^{13}\text{C}$  NMR spectrum.

We then sought to polymerize **1** using a variety of coupling methods.<sup>6</sup>  $(\text{COD})_2\text{Ni}(0)$ ,<sup>7</sup> copper(II) triflate,<sup>8</sup> and Rieke copper<sup>9</sup> failed to afford any polymeric product. Classical Ullman<sup>10</sup> coupling using copper-bronze (Aldrich) also failed when utilizing the common solvents (DMF, quinoline, tetramethylurea, or pyridine), however, in DME, copper-bronze-promoted polymerization (200°C, screw cap tube) of **1** afforded the desired polymer **2** (Scheme 1) in 56% yield after fractional precipitation ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{OH}$ ). The precipitation dramatically sharpened the polydispersity (PD) to 1.15-1.25 with  $M_n = 3\ 130$  (SEC, PS standards).<sup>11</sup> Spectral analysis again confirmed the proposed structure.

The optical spectra for **2** are most interesting. Polypyrrole has an absorption maximum of 420 nm (solid) but it is intractable. N-alkylated polypyrroles can be soluble, however, the increased steric repulsions between the consecutive aryl units causes a hypsochromic shift to approximately 380 nm.<sup>6</sup> Remarkably, the absorption maximum of **2** exhibits a strong bathochromically shifted absorbance that may be due to ionic interactions that force a diminution in the inter-unit twist angle as depicted in Scheme 1.<sup>2</sup> Solvatochromic effects are consistent with this proposal in that the following trend of  $S_0$ - $S_1$  ( $\pi\pi^*$ )

absorption maxima are present for **2**: CCl<sub>4</sub>, 520 nm; THF, 512 nm (Figure 1); EtOH/THF (1:1), 503 nm; acetone, 482

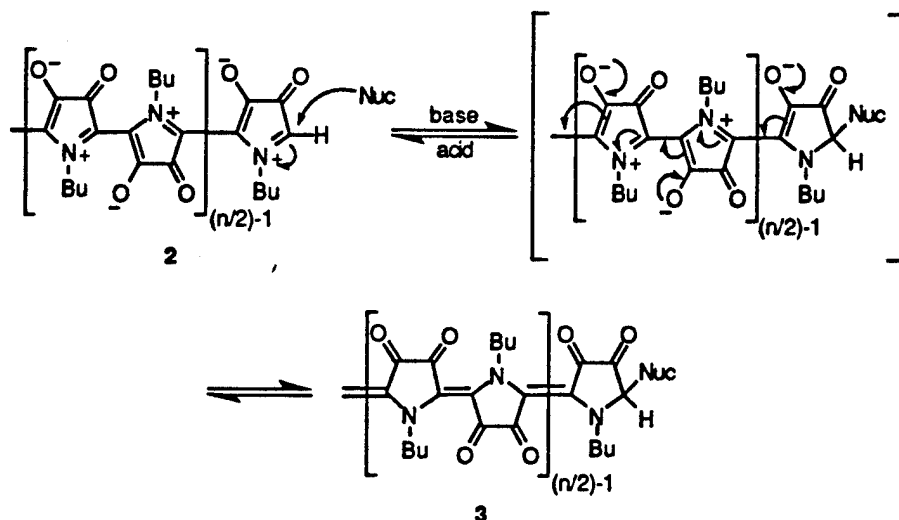
**Figure 1.** (a) Spectrum of **2** in THF (-----). (b) Dissolution of **2** in THF/aqueous NaOH to form **3** (----).

nm. Thus when the charges can be solvent stabilized, inter-unit stabilization/planarization is retarded and the absorption shifts hypsochromically. Likewise, stabilization of the polar ground state increases the energy gap of the  $\pi$ - $\pi^*$  transition which may exhibit charge transfer character.<sup>3,12</sup> Remarkably, when aqueous NaOH (0.05 M) was added dropwise to **2** in THF, the initial red-colored solution ( $\lambda_{\text{max}} = 512$  nm) became pale-orange and then finally brown ( $\lambda_{\text{max}} = 881$  nm) as more base was added (Figure 1). This pH-dependent shift in the absorption spectrum was reversible but polymer decomposition was detected after a few hours in the hydroxide-containing medium. Equally impressive solution effects occurred upon the dissolution of **2** in strongly Lewis basic solvents<sup>12</sup> such as HMPA ( $\lambda_{\text{max}} = 901$  nm) or NMP ( $\lambda_{\text{max}} = 746$  nm) (**2** was insoluble in DMSO) (Figure 2).<sup>13</sup> No polymer decomposition was

**Figure 2.** Dissolution of **2** in (a) HMPA (——) and (b) NMP (----).

detected in these Lewis basic solvents. Upon the addition of aqueous HCl, the HMPA and NMP solutions once again became red with no absorption bands present above 600 nm. The <sup>13</sup>C NMR spectrum of **2** in HMPA (with 10% CDCl<sub>3</sub> added for the lock) showed the butyl signals as well as a broad resonance from 176-163 ppm. In accord with the dramatic and reversible optical absorbance shifts, Brønsted or Lewis bases might be promoting a cascade of  $\pi$ -electron migrations in **2** to afford the planar conjugated polymer **3** (Scheme 2).

Scheme 2



Another interesting feature of **2** is that it could be partially reduced with  $\text{H}_2$  (1 atm) over Pd/C (24 h,  $23^\circ\text{C}$ ) to afford a system that is very similar to the starting polymer by FTIR, and SEC analysis, while the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR showed peak broadening; therefore, some of the units were hydrogenated. Although the reduced polymer can not attain the degree of extended conjugation of **3** (as determined by the optical absorbances), its response range to different solvents can be from the UV region with weak tailing into visible, to the near-IR (DMSO,  $\lambda = 886$  nm) (Figure 3). Thus the reduced polymer is soluble in DMSO and it responds most dramatically to solvent changes.

**Figure 3.** Spectrum of the reduction product of **2**. (a) In THF (----) and (b) in DMSO (—).

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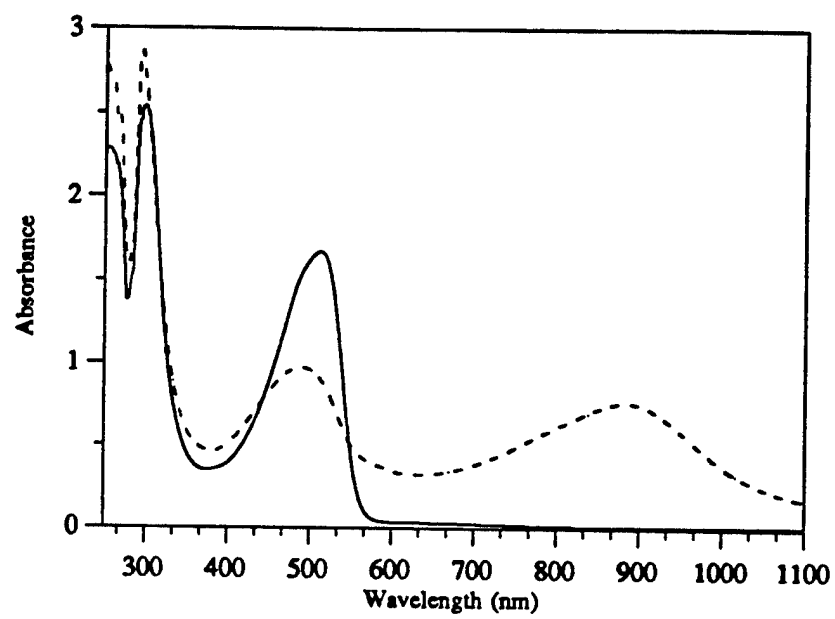


Fig 1



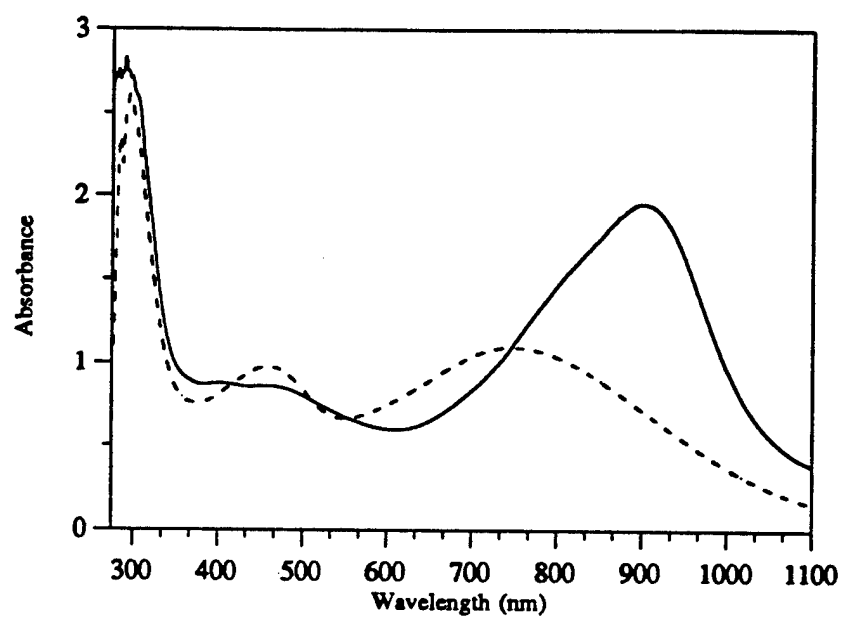


Fig 2

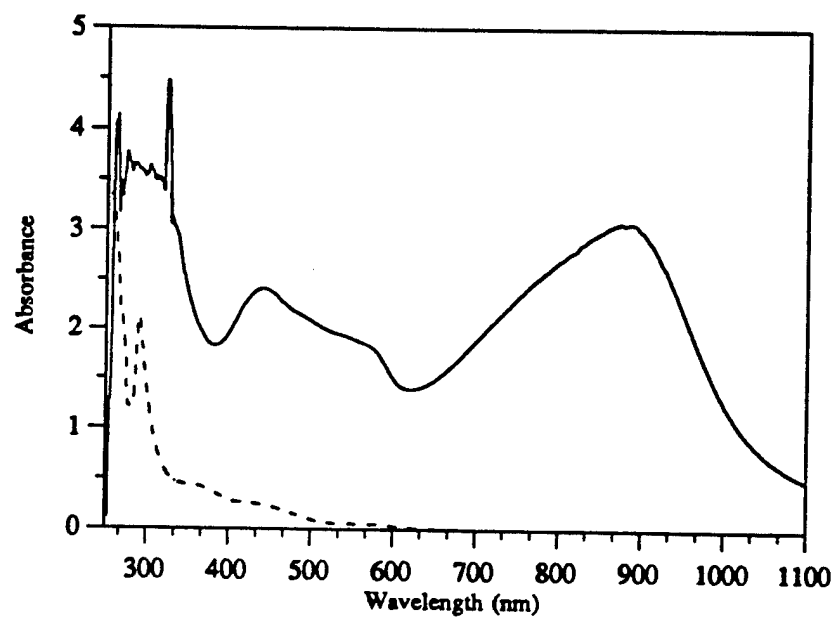


Fig 3